IDENTIFICATION OF ISOPRENOIDS, STERANES, AND TERPANES IN FISCHER ASSAY RETORTED SHALE OILS

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INTRODUCTION

In the past 15 years much work has been done on the identification of individual compounds in the branched-plus-cyclic paraffin hydrocarbon fractions from Green River oil shale bitumens; i.e., on the small amount of material that can be solvent extracted from the shale. Cummins and Robinson (1) identified the C-16, C-18, C-19, and C-20 isoprenoid alkanes. Burlingame and coworkers (2) reported the presence of C-27, C-28, and C-29 steranes. Eglinton and coworkers (3) identified cholestane, ergostane, sitostane, and perhydro-β-carotene. Anders and Robinson (4) identified 52 cyclic alkanes, and Henderson (5) identified steranes and triterpanes. Gallegos (6) identified 36 individual components in the saturate fraction of an oil shale bitumen. Robinson and Cook (7) studied the bitumen from a Wyoming oil shale core with respect to the variations in the distribution of various alkanes with stratigraphy.

Most of the geochemical studies have been made on the unpyrolyzed bitumen because of the suspicion that pyrolysis of the kerogen would destroy or alter the biological markers and thus negate the results. However, recent studies suggest that some of these markers survive pyrolysis. Gallegos (8) reported the presence of gammacerane and the C-27, C-28, and C-29 steranes in a pyrolysis study of so-called "kerogen-shale"--shale residue after the extraction of solubles with a benzene-methanol mixture. Takeo (9) reported the presence of C-18 and C-20 alkane isoprenoids in an N.T.U. shale-oil distillate.

In this study, saturate fractions of Fischer assay oils from an earlier study (10) were examined in detail to see if the biological markers survive the retorting process. A study of these biological markers in the oils produced from a core might be used as an aid in the geochemical study of sediments. Although this core is not identical to that studied by Robinson and Cook, it is from the same area so that some comparisons can be made between the bitumen and the pyrolyzed product.

EXPERIMENTAL

A core was obtained from northern Green River Basin in T21N, R107W, Sweetwater County, near Rock Springs, Wyoming. Fischer assay (11) was carried out on the sections of the core containing kerogen. A lithographic description of the core was used to composite the Fischer assay oils into 11 composite oils comprising the oil produced from adjacent shale seams of similar appearance. The 11 composite oils are representative of the three principal members of the Green River oil shale formation in this basin. The first two composite oils, L-1 and L-2, are from the Laney member; the next eight composite oils, WP-1 to WP-8, are from the Wilkins Peak member; and the last oil, T-1, is from the Tipton member, which is the lowest stratum containing kerogen.

A saturate fraction of each composite oil was prepared by dissolving 3 g of oil in approximately 10 ml of cyclohexane. The nonsaturates were removed by sulfonation and centrifugation as described in ASTM method D-1019 (12). The resulting cyclohexane-saturates solution was chromatographed on a 1/2-in. i.d. by

6-in. column packed with 60-200 mesh silica gel and eluted with bezene. Organic material was recovered by rotary evaporation of solvent.

Each saturate fraction was separated into n-paraffins and branched-plus-cyclic paraffins (BCP) by molecular sieves. The n-paraffins were recovered by destroying the molecular sieves with hydrofluoric acid (13).

All the n-paraffins and BCP fractions were analyzed using a Hewlett-Packard* 5710A gas chromatograph equipped with a flame ionization detector. Paired 50-ft by 0.02-in. i.d. support coated open tubular (SCOT) columns coated with Dexsil 300 were used. The chromatograph was programmed from 100°C at 4° per minute up to 300°C, where the temperature was maintained for 16 minutes.

Combined gas chromatography-mass spectrometry (GC-MS) of selected samples were obtained using a Hewlett-Packard 5710A gas chromatograph and an AE MS-12 mass spectrometer. A similar SCOT column was coupled directly to the source of the MS-12 without the benefit of a separator. All the mass spectra were obtained at 70 volts.

Data acquisition and processing were accomplished with a Finigan Incos 2300 series mass spectrometer data system. The magnet cycle time was 18 seconds.

RESULTS AND DISCUSSION

Geochemical investigations of biological markers are usually made on samples that have been carefully collected and preserved to prevent the formation of artifacts. However, recent work by Gallegos (8) suggests that some of the biological markers survive the retorting process, and Gallegos suggests that "The terpanes which have survived pyrolysis rather than those extracted reflect more faithfully the distribution and identity of the terpanoids originally laid down in the sediments." To investigate these possibilities, we examined the alkane hydrocarbons in oils produced by retorting oil shales from different geologic regimes. All the shales were retorted in identical fashions by Fischer assay which heats the shale at a controlled rate to 500°C.

Geology

A brief description of the geology of the area from which the subject core was obtained will set the stage for the discussions. The oil shales of the Green River Formation in Wyoming were formed in Gosiute Lake in early and middle Eocene age (14). This lake went through three major changes in size. During the first stage, in which the Tipton member was laid down, it was large and overflowing, and thus a fresh water lake. During the second, or Wilkins Peak stage, the lake shrank and became extremely saline. When the top, or Laney member, was laid down the lake had again expanded, overflowed, and become a fresh water lake.

General Characteristics

Table 1 shows the depth and length of the sections that were composited for Fischer assay, together with the oil yield, the percent of total saturates, and the percents of this saturate fraction that are normal and branched-plus-cyclic paraffins (BCP). The lengths of the core vary from 193 feet for WP-6 to 7 feet for T-1, showing considerable difference in the length of the homogeneous bands. The oil yield data show that the oil shale in this area is lean, ranging from 4.5 to 15.9 gallons per ton. The average yield for the core, excluding the barren sections, (most of which are in the top 300 feet) is 9.0 gallons per ton. The

*Mention of specific brand names or models of equipment is for information only and does not constitute an endorsement by the Department of Energy.

saturates represent 9 to 11 percent of all the oils except the Tipton, the single sample of which has a somewhat higher saturate content than the other oils. A previous study (10) showed that the Tipton oil had significantly smaller amounts of polar compounds than the other oils. Thus, its high content of paraffins may simply reflect a lack of dilution by the polar components.

TABLE 1. - Description of Wyoming core and percentages of saturates, normal, and branched-plus-cyclic hydrocarbons in the Fischer assay oils

Section[1]	Depth[1] ft.	Length[2] ft.	Yield, gal/ton	Saturates, vol. % of oil	Vol % of saturates	
					n-paraffins	Branched-cyclic paraffins
L-1	771.5	38.1	5.3	9.7	63.9	36.1
L-2	870.5	59.6	10.3	11.1	60.4	39.6
WP-1	1064.7	44.3	13.5	8.9	39.3	60.7
WP-2	1109.0	48.6	15.1	9.7	46.4	53.6
WP-3	1157.6	41.2	11.0	10.2	45.1	54.9
WP-4	1250.0[4]	26.4	8.0	9.8	48.0	52.0
WP-5	1276.4	45.6	15.9	9.7	51.5	48.5
WP-6	1322.0	193.0	6.1	9.9	39.4	60.6
WP-7	1515.0	101.0	8.9	9.8	51.0	49
WP-8	1616.0	94.0	7.3	10.0	56	44
T-1	1710.0	7.0	4.5	13.3	63.9	36.1

[1] L = Laney member, WP = Wilkins Peak member, T = Tipton member

[2] Top of section

[3] Excluding barren section

[4] 51.2 feet of core missing between WP-3 and WP-4

Normal Paraffins

Table 1 shows variations in the composition of the saturate fractions with regard to their content of n-paraffins. The Laney and Tipton saturates are 60 to 64 percent n-paraffin, while the Wilkins Peak saturates contain significantly lower amounts. Thus, the two freshwater deposits are higher in n-paraffins than the saline deposit. The high value of WP-8, which is adjacent to the Tipton core, may suggest an influence of the freshwater member on its adjacent saline member; i.e., a somewhat gradual transition from fresh to saline.

Gas chromatographic investigation of the n-paraffin fractions of the 11 oils shows n-paraffins from C-11 to C-34 with the greatest abundance at about C-17. The odd-to-even preference that was noted in n-paraffin fractions of bitumens from a similar core (7) is absent. This result was not unexpected in these oils, which had been heated at 500°C, because Cummins (15) showed disappearance of the odd-to-even preference when shales were degraded at temperatures of 150 to 350°C.

Branched-Plus-Cyclic Paraffins

Gas chromatograms of the BCP fraction of the oils suggested the presence of chain isoprenoids, steranes, and pentacyclic triterpanes. Chromatograms of samples from each of the members are shown in Figure 1. Combined GC-MS analyses were obtained on these three representative fractions to identify the major peaks. An example of the resulting reconstructed chromatograph for the Wilkins Peak sample is shown in Figure 2. Two of the peaks--26 and 31--contained two compounds, while each of the others contained one. Thirty-six compounds were identified in the GC

fractions and accounts for 55 percent of the BCP fraction. In several instances, as will be noted later, the MS identification was confirmed by coinjection of authentic samples. The qualitative data from the mass spectra may now be combined with the quantitative data from gas chromatography to examine the various types of compounds that are present in these oils.

Chain Isoprenoids. - The larger peaks in the first part of the gas chromatograms (Figure 1) are chain isoprenoids. The GC peak number and the empirical formula of these compounds are listed in Table 2. The gas chromatographic data in Figure 1 show considerable variation in the amounts of the individual isoprenoids. Phytane (peak 14) increases from 2 percent in the Tipton to 5.5 in the Wilkins Peak and to 8.3 in the Laney. This increase in a compound usually thought to be a degradation product of chlorophyll (4) may suggest an increase in the amount of vegetative matter as the lake went from the Tipton to Wilkins Peak to Laney.

TABLE 2. - Chain isoprenoids (C_nH_{2n+2}) identified

GC peak no.	Empirical formula	Molecular weight	Common name
1	$C_{13}H_{28}$	184	
2	$C_{14}H_{30}$	198	
4	$C_{15}H_{32}$	212	Farnasane
6	$C_{16}H_{34}$	226	
8	$C_{17}H_{36}$	240	
10	$C_{18}H_{38}$	254	
12	$C_{19}H_{40}$	268	Pristane
14	$C_{20}H_{42}$	282	Phytane
15	$C_{21}H_{44}$	296	
15A	$C_{22}H_{46}$	310	
16	$C_{23}H_{48}$	324	
17	$C_{24}H_{50}$	338	
18	$C_{25}H_{52}$	352	
19	$C_{30}H_{62}$	412	Squalane

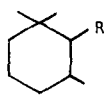
Inspection of Figure 1 reveals many differences in the ratios of the amounts of the chain isoprenoids. For example, the ratio of the heights of peaks 10, 12, and 14 changes from 1.2/1.0/2.4 to 1.2/1.0/1.3 to 0.8/1.0/1.0 as the depth increases.

Monocyclic Isoprenoids. - Eight monocyclic isoprenoids shown in Table 3 were identified, These are the small, odd-numbered peaks in the first part of the chro-

TABLE 3. - Monocyclic isoprenoids (C_nH_{2n}) identified

GC peak no.	Empirical formula	Molecular weight
3	$C_{14}H_{28}$	196
5	$C_{15}H_{30}$	210
7	$C_{16}H_{32}$	224
9	$C_{17}H_{34}$	238
11	$C_{18}H_{36}$	252
13	$C_{19}H_{38}$	266
18A	$C_{29}H_{58}$	406
32	$C_{40}H_{78}$	558

matograms (Figure 1) and 18A in the chromatogram of T-1. These compounds have the empirical formula C_nH_{2n}, and the general structure



where R is a saturated chain of varying length. The amounts of these compounds, which are thought to be derived from perhydro-β-carotene, are small so that quantitative differences are obscured except for the C-29 compound (peak 18A). This compound makes up 2.3 percent of the BCP fraction of the Tipton but is absent in the Wilkins Peak and the Laney. The mass spectrum of this compound shows fragments that are typical of monocyclic isoprenoids.

Dicyclic Isoprenoid--Perhydro-β-Carotene. - A dicyclic compound, peak 32 in Figure 1, was shown to be perhydro-β-carotene. The parent molecular ion observed in the mass spectrum of this component was at m/g = 558. Diagnostic fragment ions in the spectrum occurred at m/g = 125, 137, and 502. These ions have been noted in the mass spectrum of perhydro-β-carotene (6). The identity of component 32 was verified by coinjection of an authentic sample.

Steranes. - The steranes identified in the BCP fractions of the retorted oils are shown in Table 4. The compounds were identified by comparing mass spectra with published spectra and by coinjection in the case of the two cholestanes. All of these compounds have been identified in shale oil bitumen by Gallegos (6), Eglinton (3), Henderson (5), and others.

TABLE 4. - Sterane (C_nH_{2n-6}) compounds identified

GC peak no.	Empirical formula	Molecular weight	Common name
20	$C_{27}H_{48}$	372	5-β-cholestane
21	$C_{27}H_{48}$	372	5-α-cholestane
22	$C_{28}H_{50}$	386	5-β-ergostane
23	$C_{28}H_{50}$	386	5-α-ergostane
24	$C_{29}H_{52}$	400	5-β-stigmastane
25	$C_{29}H_{52}$	400	5-α-stigmastane
26[1/]	$C_{30}H_{54}$	414	unknown

[1/] Peak contains two compounds, one of which is a tetracyclic terpane, the other a pentacyclic triterpene of mass 398

The amounts of these compounds vary greatly, as shown in Figure 1. The Wilkins Peak samples contain more 5-α-ergostane (peak 23) and 5-β-stigmastane (peak 25) than either the Laney or the Tipton samples. A comparison of these peaks in the 11 samples shows three times as much α-ergostane and about four times as much α-stigmastane in the Wilkins Peak samples as in the Laney or Tipton samples. This, again, indicates that the sedimentary deposition during the Wilkins Peak time was different than during the Laney or the Tipton time.

The ratio of the abundance of the 5-α- to the 5-β- isomers of all three steranes--cholestane, ergostane, and stigmastane--was approximately 3 to 1, similar to that found by Gallegos (6) in oil shale bitumen. Thermodynamically, the more stable isomer is the alpha form, and the above results indicate that exposure to 500°C during the retorting step does not change the ratio of the alpha to beta isomers.

Pentacyclic Triterpanes. - The pentacyclic triterpanes identified are listed in Table 5. The structures of these compounds are shown in Figure 3. All of these compounds have been previously identified (4, 6, 7). Peak 26 contains two compounds. One is a pentacyclic triterpane with a molecular weight of 398; the mass spectrum of this compound is similar to the pentacyclic triterpane D reported by Whitehead (16) and by Gallegos (6) as compound 30. The peak labeled 27, Figure 3, is believed to be an isomeric form of the compound that emerged as part of peak 26. It was not possible to determine the position of the methyl group in the E ring of peak 27 from the fragmentation pattern. Peaks 28 and 29 are believed to be isomeric compounds with the structure shown in Figure 3. It was not possible to identify the position of the propyl group in these compounds, one of which may be hopane, as suggested by Henderson (5). Peaks 30 and 31 are apparently isomeric pentacyclic triterpanes, with the structures shown in Figure 3.

TABLE 5. - Pentacyclic triterpanes (C_nH_{22-8}) identified

GC peak no.	Empirical formula	Molecular weight
26[1/]	$C_{29}H_{50}$	398
27	$C_{29}H_{50}$	398
28	$C_{30}H_{52}$	412
29	$C_{30}H_{52}$	412
30	$C_{31}H_{54}$	426
31[2/]	$C_{31}H_{54}$	426

[1/] Peak contains two compounds, one of which is a pentacyclic triterpane, the other a tetracyclic terpane with a molecular weight of 414.

[2/] Peak contains two compounds, one of which is gammacerane, and an unidentified pentacyclic triterpane.

Semi-Quantitative Comparisons

Table 6 presents semi-quantitative data on some of the types of compounds in the BCP fraction. The data were obtained by integrating the areas under the chro-

TABLE 6. C-13 to C-20 chain isoprenoids, α-steranes, and perhydro-β-carotene in the branched-cyclic fraction of the retorted oils

	Vol % in branched-plus-cyclic fraction[1/]		
Section	Chain isoprenoids	α-Steranes	Perhydro-β-carotene
L-1	16.9	2.9	0.8
L-2	21.0	4.9	1.3
WP-1	17.7	8.8	1.4
WP-2	26.5	8.2	0.9
WP-3	25.2	5.2	1.0
WP-4	25.4	8.5	0.7
WP-5	23.6	6.0	1.4
WP-6	23.0	6.7	1.2
WP-7	20.4	8.3	1.4
WP-8	17.4	5.4	2.1
T-1	10.5	2.6	0.5
Oil average	20.7	6.1	1.1
Bitumen average[2/]	29.9	14.1	4.6

[1/] Area percentages calculated from FID chromatogram

[2/] Data from Cook and Robinson (7)

matographic peaks for perhydro-β-carotene and for the C-13 to C-20 compounds listed in Table 2 and the α-steranes in Table 4. The data are semi-quantitative because of the difficulty in establishing a baseline. No attempt was made to integrate the small peaks for monocyclic isoprenoids and β-steranes. In general the table shows lower amounts of chain isoprenoids, α-steranes, and perhydro-β-carotene in the samples from the Laney and the Tipton member than in the Wilkins Peak samples. This suggests that the sedimentary deposition during the Laney and the Tipton time was different than during the highly saline period of the Wilkins Peak time.

Table 6 also shows the average of chain isoprenoids, α-steranes, and perhydro-β-carotene for the 11 oils and a similar calculation on the bitumen samples studied by Robinson and Cook (7). The BCP fraction of the bitumen contains 1.4 times more chain isoprenoids, about twice the amount of α-steranes, and about 4 times more perhydro-β-carotene than the retorted samples.

CONCLUSIONS

Biological markers have been identified in shale oil produced by Fischer assay retorting of oil shale. The biological markers identified include isoprenoid alkanes, monocyclic terpanes, steranes, and pentacyclic triterpanes. These are the same classes of compounds that have been identified in extracted bitumen and pyrolyzed oil shale. The results from this study do not indicate the source of these compounds in oil shale. These compounds probably represent material from both the bitumen and kerogen.

The distribution of these compounds in the different sedimentary layers varies considerably. The data show little if any influence of depth-related factors, a conclusion similar to that drawn from a study (7) of the bitumen from a Wyoming core. Although the phytane appears to decrease with increasing depth, this may be due to an increase in the amount of vegetative (chlorophyll-bearing) matter as the lake went from the Tipton to the Laney era. In agreement with the bitumen data of Robinson and Cook, we found that the Laney (top) and the Tipton (bottom) member samples were usually similar and had a somewhat lower quantity of isoprenoids, steranes, etc., than the Wilkins Peak (middle) member samples. This difference is probably due to the differences in environment, that is, fresh water lake during the Laney and Tipton eras and a salt water lake during the Wilkins Peak era.

The chain isoprenoid content in the BCP fractions from the 11 retorted oils average approximately 21 percent, and Robinson and Cook's results for the bitumen on their core were about 30 percent. Although direct comparisons cannot be made because their work was on a different core and on the extracts of the oil shale from the core, our results appear to indicate that the chain isoprenoids are stable to the retorting process. The chain isoprenoids averaged approximately 19 percent for the Laney, 23 percent for the Wilkins Peak, and 10 percent for the Tipton samples. This difference in the amount of these isoprenoids in the three member samples points out again the difference in the environment in the Gosiute Lake during the formation of these three members.

For the most part, previous studies of the biological markers in oil shale have dealt with the material extracted from bitumen. Gallegos had indicated that the material produced from the pyrolysis of oil shale may be more indicative of the biological source material than extracted bitumen (6). We feel that both the material from extracted bitumen and the product oil should be investigated for a more complete geochemical picture of oil shale formation.

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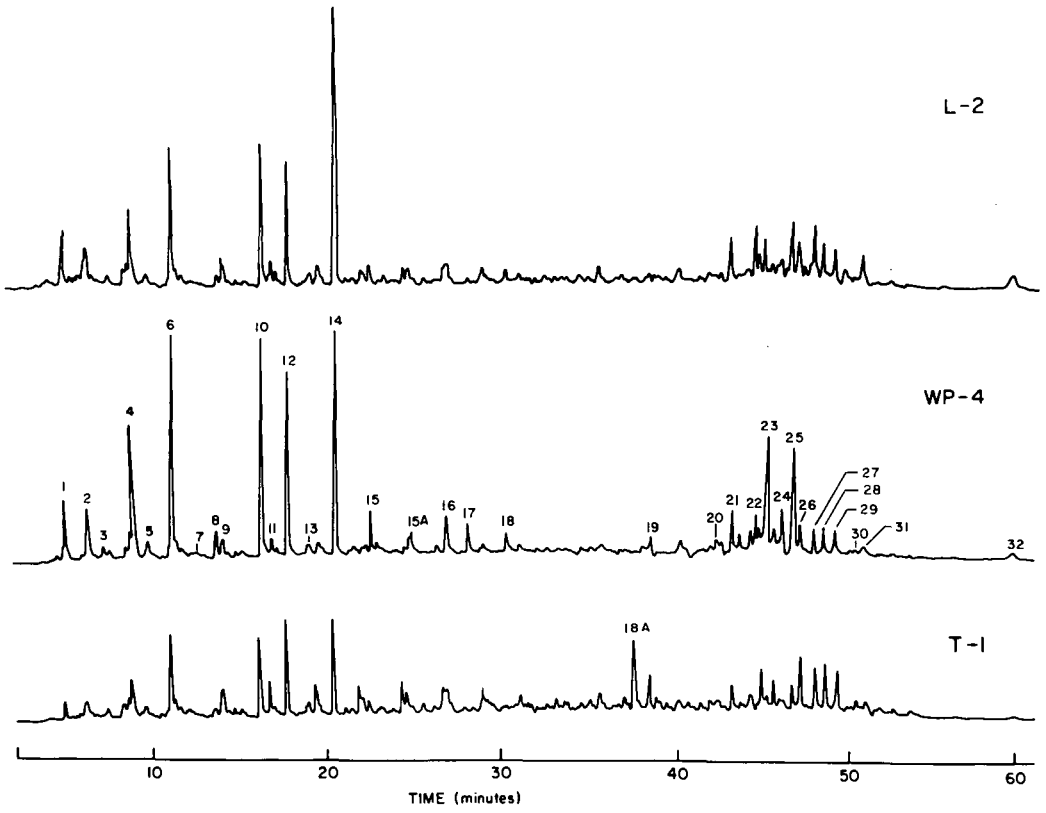


FIG. 1. GAS CHROMATOGRAPHS (FID) OF THE BRANCHED-CYCLE HYDROCARBON FRACTION FROM RETORTED WYOMING SHALE OIL.

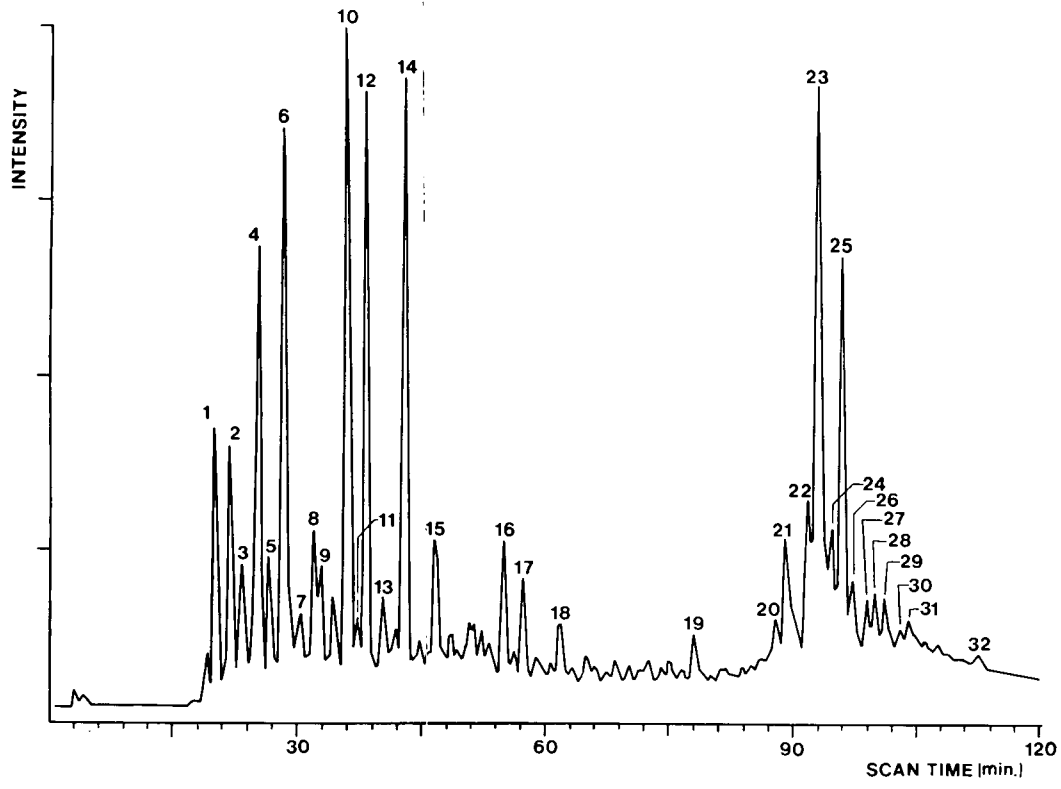
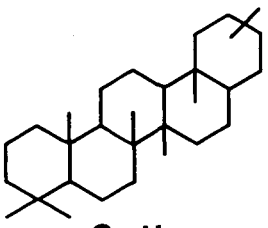
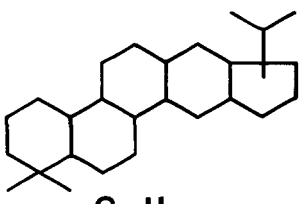


FIG. 2. RECONSTRUCTED GAS CHROMATOGRAPH OF BRANCHED-CYCLE HYDROCARBON FRACTION FROM WP-4 RETORTED WYOMING SHALE OIL.



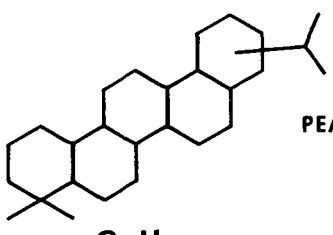
PEAK NO. 26 & 27

$C_{29}H_{50}$



PEAK NO. 28 & 29

$C_{30}H_{52}$



PEAK NO. 30 & 31

$C_{31}H_{54}$

FIG. 3. PENTACYCLIC TRITERPANES IN GREEN RIVER RETORTED SHALE OIL